New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni–Cd batteries by solvent extraction

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Abstract

A new solvent extraction flowsheet for recovery of cadmium, cobalt and nickel in pure and marketable forms from sulphate solutions is proposed. The solutions processed were equivalent to those expected from sulphuric acid leaching of Ni–Cd–Co-containing residues and of spent rechargeable batteries, assaying about 80 g/l Ni, 30 g/l Cd and 1–3 g/l Co. In the new process proposed the metals are separated in two solvent extraction circuits: the cadmium separation circuit where the organophosphoric acid DEHPA (1 M) is used as extractant and the cobalt separation circuit where the organophosphinic acid Cyanex 272 (0.5 M) is the extractant. It is demonstrated that these two extractants are more efficient and selective than other competitors, namely the organophosphonic acid Ionquest 801. Under optimised conditions 99.7% of the cadmium can be recovered in the first circuit. After scrubbing of the loaded DEHPA with a pure cadmium solution this metal can be stripped into an aqueous phase assaying 195 g/l Cd, 0.14 g/l Co and 0.04 g/l Ni. The raffinate from cadmium separation is further processed in the cobalt circuit. A recovery of 99.5% of the cobalt can be attained in this second circuit. After scrubbing the loaded Cyanex 272 with a pure cobalt aqueous solution, the cobalt is stripped generating strip liquor with 126 g/l Co, 0.07 g/l Ni and 0.05 g/l Cd. The production of pure and marketable chemicals dictated the solvent extraction strategy and the conditions selected for the separation process proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cadmium; Cobalt; Nickel; Extraction; Recovery; Separation; Batteries; Residues

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1. Introduction

Solvent extraction has been widely used in extractive metallurgy for metals recovery and purification. This technology has been proposed also for waste treatment and recycling, as are the cases of the MAR process for copper, zinc and nickel residues [1], the processing of electric arc furnace dusts [2,3] and metals recovery from spent catalyst [4,5].

In the particular case of metals recovery from Ni–Cd spent batteries most of the processes reported in literature are essentially pyrometallurgical, such as the SAB NIFE [6], the SNAM [7] and the INMETCO [8] processes, all of them in use. These processes are essentially based on cadmium recovery by distillation around 900°C. They are in fact very efficient concerning the management of Ni–Cd residues since they are capable of solving the main related environmental problem: the release of the contained cadmium. Nevertheless, the most valuable heavy metals (cobalt and nickel) are not usefully recovered. Furthermore, pyrometallurgical operations are strongly energy-consuming and some emissions of dust and gases are expected.

So, several hydrometallurgical processes have been developed for the treatment of spent primary and secondary batteries. The TNO process for Ni–Cd batteries uses hydrochloric acid leaching followed by the separation of cadmium chloride complexes by solvent extraction with TBP [9]. Both nickel and cadmium are recovered separately by electrowinning. Bartolozzi et al. [10] developed a method for recovery of metals from Ni–Cd batteries using sulphuric acid leaching followed by cadmium recovery by selective electrowinning. Lyman and Palmer [11] investigated the recycling of nickel–metal hydride batteries using hydrometallurgical operations such as solvent extraction with DEHPA. Zhang et al. also presented treatment alternatives by hydrometallurgy for the recovery of metal values from lithium-ion [12] and nickel–metal hydride [13] spent batteries. The BATENUS process provides a global solution for the treatment of mixed battery waste, using sulphuric acid leaching and a combination of ion exchange and solvent extraction for metals purification [14]. Solvent extraction is therefore used by several authors as the most efficient separation technology for the treatment of these types of residues.

It must be stressed that cadmium, cobalt and nickel separation from leaching solutions by solvent extraction is not a common challenge. In extractive metallurgy, cadmium is usually associated with zinc in mineral deposits while cobalt and nickel are associated with copper.

Practical examples of cadmium extraction are not abundant. Some references can be found where this metal is processed together with other metals such as zinc [15]. Ritcey [16] demonstrated the possibility of cadmium–nickel separation from leachates of Ni–Cd sludges using the ammonium salt of DEHPA. In a recent study Owusu [17] showed the feasibility of the selective extraction of zinc and cadmium over cobalt and nickel also with DEHPA. In the above process, after zinc separation, cadmium was selectively extracted at pH 3.7 with very low contamination of cobalt and nickel.

Cobalt and nickel separation in sulphate medium by solvent extraction has been extensively studied and some industrial plants have already been operated. Ritcey developed the first process using DEHPA in the early 70's [18]. The process was

adapted and operated at the Hitachi plant in Japan, at the Sudbury complex in Canada and at Matthey Rustenburg refinery in South Africa, as referred to by Preston [19]. The main drawbacks of the process were the poor selectivity at high Ni:Co ratios and the high temperature used (above 50°C). Efforts were made to synthesize more selective agents for cobalt over nickel, namely phosphonic and phosphinic acids [19–24], which have been developed and successfully commercialised to substitute DEHPA in cobalt/nickel separation plants.

This paper reports in detail the studies carried out to define conditions and parameters for cadmium, cobalt and nickel separation by solvent extraction. The work is part of a project on the development of a hydrometallurgical process in sulphate medium for spent Ni–Cd battery recycling, which was succinctly presented elsewhere [25]. The main features of that process are (1) mechanical processing by shredding and separation of battery fractions; (2) leaching of electrode fractions with sulphuric acid, a cheap reagent and less corrosive than other acids; (3) cadmium, cobalt and nickel separation by solvent extraction; (4) metals recovery from the separated streams by electrodeposition or crystallisation as sulphates and (5) separation of case materials (nickel, iron, plastic) free of cadmium for further recovery.

The arrangement proposed here is a new approach for Ni–Cd batteries recycling since none of the existing processes involve cobalt recovery. Cobalt is a valuable metal in the cathodes that is not recovered in other processes despite its commercial value.

Hydrometallurgy applied to Ni–Cd spent batteries recycling is versatile enough to be used to treat other similar waste materials such as nickel-containing sludge or dusts and spent catalysts. Solvent extraction can even play a crucial role, allowing the manufacture of high purity products.

2. Experimental

2.1. Solutions and reagents

In this work aqueous pregnant solutions were used containing nickel, cadmium and cobalt in similar concentrations to those leaving the leaching step of the above noted hydrometallurgical process for Ni–Cd batteries recycling [25]. Typical values considered were 80 g/l Ni, 30 g/l Cd and 1–3 g/l Co. In the case of cobalt the concentration adopted in the range 1–3 g/l depended on the proportion batteries/sludges to be treated by the process. The solutions used were made by dissolution of the respective sulphates (reagent grade, extra pure, from Riedel-de Haën) in distilled water. For acidity or pH adjustment, sulphuric acid p.a. and sodium hydroxide r.g. were used.

Albright and Wilson Americas kindly supplied the extractants DEHPA—di (2-ethylhexyl) phosphoric acid, and Ionquest 801—2-ethylhexyl phosphonic acid mono (2-ethylhexyl ester). Cytec Canada provided the extractant Cyanex 272—bis (2,4,4-trimethyl pentyl) phosphinic acid, 85% pure. The extractants were used as received without further purification. The diluents used were Shell D70 (aliphatic) for the cases of DEHPA and Ionquest 801, and Exxon Escaid 102 (14% aromatics) for Cyanex 272. The use of the partially aromatic diluent for the phosphinic acid was due to the fact that

selectivity Co/Ni is improved by the aromatic content of the diluent. No modifiers were used since no problems were found concerning phase separation behaviour. After the preparation of the extractants, the concentrations were rigorously determined by potentiometric titration in alcoholic media with a standard soda solution.

2.2. Solvent extraction procedures

The aqueous and organic phases were contacted at the desired organic/aqueous (O/A) volume ratios for 20 min. This time was found long enough to attain the equilibrium as verified in preliminary tests. The phases were mixed in separatory funnels using an orbital shaker or alternatively in a glass cylindrical reactor provided with an impeller agitator (600 min^{-1}). This second option was used in the experiments where the pH was controlled through the addition of a few drops of a soda solution. Experiments were always carried out at room temperature $(22 \pm 2°C)$. After contact, the phases were allowed to settle, separated and filtered (filters Whatman No. 52 for aqueous phases and 1 PS for organic phases).

2.3. Analytical methods

The concentrations of cadmium, nickel and cobalt in the aqueous phases were determined by atomic absorption spectrometry (AAS) or, alternatively, by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The concentrations in the organic phases were determined by complete stripping of the organics with sulphuric acid 2 M and subsequent analysis of the aqueous strip liquors obtained. The maximum analytical errors associated with the concentrations, estimated by statistical methods, were 2.5% for cadmium, 3% for nickel and 4% for cobalt. The accuracy of the analytical methods was checked by mass balance in the two phases and the maximum deviations permitted were 5%.

3. Selection of extractants and optimisation of conditions

3.1. Selection of extractants

The first series of tests was performed with a diluted solution containing 1 g/l of each metal (Cd, Ni and Co) and using 1 M DEHPA and 1 M Cyanex 272 as extractants. In this particular case sodium sulphate was added to the aqueous solution (0.3 M in Na_2SO_4) to avoid phase separation problems related to the low ionic strength. These experiments envisaged realising the chemical behaviour of these systems in very favourable extracting conditions. The influence of pH on the extraction efficiency is presented in the Fig. 1. The order of extraction found for both extractants was $Cd > Co > Ni$ and it is clear that the phosphoric acid is more efficient since it is capable of extracting all the metals at lower pH values. Regarding the selectivity, DEHPA is
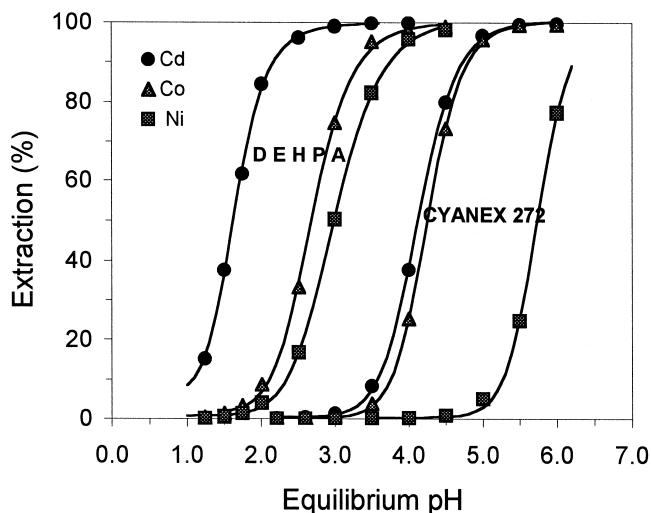
Fig. 1. Extraction efficiency of Cd, Ni and Co (1 g/l in initial aqueous) against equilibrium pH for the extractants 1 M DEHPA and 1 M Cyanex 272; O/A = 1.

very selective for cadmium while Cyanex 272 is not, due to the proximity of the Cd and Co curves. In contrast, after cadmium removal, the phosphinic acid allows efficient separation of cobalt from nickel, as expected. The quantification of these discussions is made in Table 1 where the $pH_{1/2}$ values for the several metals and the respective differences are presented.

The separation factors β were calculated and are plotted against pH in Fig. 2. It is clearly demonstrated that Cyanex 272 is suitable for cobalt/nickel separation (maximum $\beta_{Co/Ni} = 540$ at pH 5.5). The capacity of this extractant to separate cadmium from nickel in the absence of cobalt is also apparent. Separation factors for DEHPA are less dependent on pH. In the range pH 1.5 to 3 the separation of cadmium is achieved with values of $\beta_{Cd/Ni} = 110$ and $\beta_{Cd/Co} = 45$.

The results obtained suggest a separation process composed of two separate circuits where in the first cadmium can be selectively extracted by DEHPA and in the second the cadmium-free raffinate can be subsequently processed with Cyanex 272 for cobalt/nickel separation. To evaluate the application of this principle to the real

Table 1
pH for 50% extraction ($pH_{1/2}$) and respective differences ($\Delta pH_{1/2}$) for solutions with 1 g/l of each metal

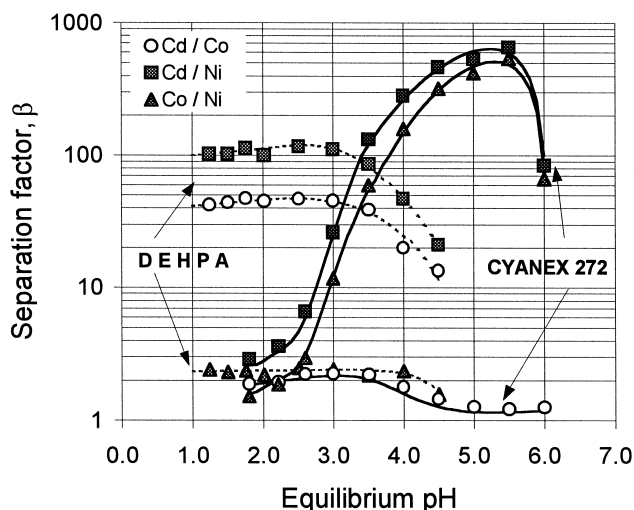| Extractant	$pH_{1/2}$			$\Delta pH_{1/2}$		
	Cd	Co	Ni	Co–Cd	Ni–Cd	Ni–Co
1 M DEHPA	1.62	2.68	2.99	1.06	1.37	0.31
1 M Cyanex 272	4.12	4.25	5.73	0.13	1.61	1.48

Fig. 2. Separation factors against equilibrium pH for the extractants 1 M DEHPA and 1 M Cyanex 272 with diluted metal solutions (1 g/l in initial aqueous); O/A = 1.

solutions coming from the leaching of the battery fractions, a new series of experiments were performed with typical leach solutions at selected pH values. The phosphonic acid Ionquest 801 was also included in this series of tests to evaluate its potential value in the separation process.

Concerning the cadmium separation, Table 2 shows the extraction efficiency and the separation factors obtained with 1 M DEHPA and 1 M Ionquest 801 from an aqueous solution containing 80 g/l Ni, 30 g/l Cd and 3 g/l Co. The separation of cadmium from cobalt is better achieved with DEHPA since in all the pH range tested cadmium recovery is always higher and the cobalt co-extraction is always lower when using the alkylphosphoric acid. This fact is also confirmed by the separation factor values. Regarding nickel it is clear that the lower extraction values and the higher separation

Table 2

Extraction of Cd, Co and Ni and separation factors at selected pH values with DEHPA and Ionquest 801 from aqueous concentrated solutions containing 80 g/l Ni, 30 g/l Cd and 3 g/l Co; O/A = 1

| pH	Extractant	% Extraction			$\beta_{Cd/Co}$	$\beta_{Cd/Ni}$
		Cd	Co	Ni		
2.0	1 M DEHPA	32	0.3	0.1	71	370
	1 M Ionquest 801	13	0.4	0.1	53	130
3.0	1 M DEHPA	67	5	1.3	42	148
	1 M Ionquest 801	52	7	0.2	15	600
4.0	1 M DEHPA	82	20	7	18	62
	1 M Ionquest 801	75	26	0.5	9	680

factors $\beta_{Cd/Ni}$ are obtained with the alkylphosphonic acid indicating that this agent is better with respect to the separation of cadmium from nickel. Taking into account that the extraction order is Cd > Co > Ni it is obvious that the main contaminant in the cadmium separation circuit is cobalt. So, in a global appreciation it can be concluded that the extractant DEHPA will provide a more efficient separation of cadmium from the other two metals. It is however important to stress that Ionquest 801 is also a good alternative.

After cadmium removal the separation of cobalt from nickel can be achieved with Cyanex 272. Table 3 shows the extraction efficiencies obtained with typical pregnant solutions from which cadmium has presumably been extracted, i.e., containing 80 g/l Ni and 3 g/l Co. Ionquest 801 was again used for comparison purposes. The extractant concentrations were here reduced to 0.5 M to improve the selectivity. Both the cobalt extractions and the separation factors are undoubtedly favourable for the case of the alkylphosphinic acid, as expected.

A separation process based on two circuits can be proposed: (1) the cadmium separation circuit in which cadmium is extracted with DEHPA and (2) the cobalt separation circuit where cobalt and nickel are separated with Cyanex 272. The phosphonic acid Ionquest 801 also showed very interesting behaviour since it can be used in both circuits despite having lower separation efficiencies. Nevertheless, it was decided to adopt the most efficient solution.

3.2. Optimisation of extraction conditions

The optimisation of the extraction conditions was essentially carried out in terms of extractant concentrations and pH. In the cadmium circuit the concentration selected for DEHPA was 1 M. Concentrations below 1 M are unsuitable since this value is very close to the stoichiometric quantity predicted from the extraction equation below,

$$M^{2+}_{(aq)} + 2(HA)_{2(org)} = M(HA_2)_{2(org)} + 2H^+_{(aq)} \tag{1}$$
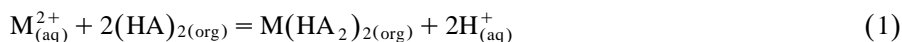
where M represents the metal and $(HA)_2$ the dimeric form of the organic acid. For O/A = 1 and for a cadmium concentration of 30 g/l (0.27 M), the stoichiometric

Table 3
Extraction of Co and Ni and separation factors at selected pH values with Cyanex 272 and Ionquest 801 from aqueous concentrated solutions containing 80 g/l Ni and 3 g/l Co; O/A = 1

pH	Extractant	% Extraction		$\beta_{Co/Ni}$
		Co	Ni	
4.0	0.5 M Cyanex 272	17	0.1	204
	0.5 M Ionquest 801	45	2	38
5.0	0.5 M Cyanex 272	90	0.8	1100
	0.5 M Ionquest 801	89	7	98
5.5	0.5 M Cyanex 272	97	2	1260
	0.5 M Ionquest 801	91	10	96

concentration of $(HA)_2$ is 0.53 M, equivalent to 1.06 M of the free extractant HA. Some tests not reported in this paper were performed at lower DEHPA concentrations and a marked decrease was found in cadmium loading. Concentrations of DEHPA over 1 M are not appropriate due to its viscosity and related problems in phase disengagement.

In the case of the cobalt circuit four concentrations of Cyanex 272 were tested, at constant pH of 5 (Table 4). The evaluation of the results was made in terms of the extraction efficiency and selectivity in a single contact $(O/A = 1)$ and also by determining the loading capacity in three successive contacts of the same organic phase with fresh aqueous phases at $O/A = 1/3$. The use of the lower concentration (0.1 M) led to a substantial decrease in cobalt extraction while the highest concentration (0.75 M) caused a loss of selectivity Co/Ni since the nickel extracted is practically three times higher with a very small change in the cobalt recovery. Concerning the two intermediate concentrations it can be said that the use of 0.5 M extractant allows an organic loading capacity of 4.5 g/l Co compared with 2.5 g/l Co when using 0.25 M. The concentration of 0.5 M for Cyanex 272 was therefore selected for further work.

In the cadmium circuit, the maximisation of the extraction differences ΔE below implies the optimisation of the extraction pH,

$$\Delta E_{Cd-Ni} = E_{Cd} - E_{Ni} \tag{2}$$

$$\Delta E_{Cd-Co} = E_{Cd} - E_{Co} \tag{3}$$

E refers to the extraction percentage for each pH value. According to this criterion the optimum pH value for the separation of cadmium from cobalt was 3.5 while 4.0 was the optimum pH found to achieve better separation of cadmium from nickel (Fig. 3). The pH 3.5 was selected as the optimum value to adopt, whereas it was concluded that cobalt is the major interfering element in the cadmium separation circuit.

The separation factors $\beta_{Cd/Ni}$ and $\beta_{Cd/Co}$ were determined (Fig. 4). Comparing these factors with those obtained with diluted solutions (Fig. 2) an increase can be observed which indicates that selectivity for cadmium is better at higher metal concentrations.

The same study was made for the cobalt circuit. The extractant used was 0.5 M Cyanex 272 and the pH range tested was from 3 to 6.5. In this case two aqueous

Table 4
Influence of the extractant concentration on the extraction efficiency and on the selectivity Co/Ni for an initial aqueous solution containing 80 g/l Ni and 3 g/l Co; pH = 5.0

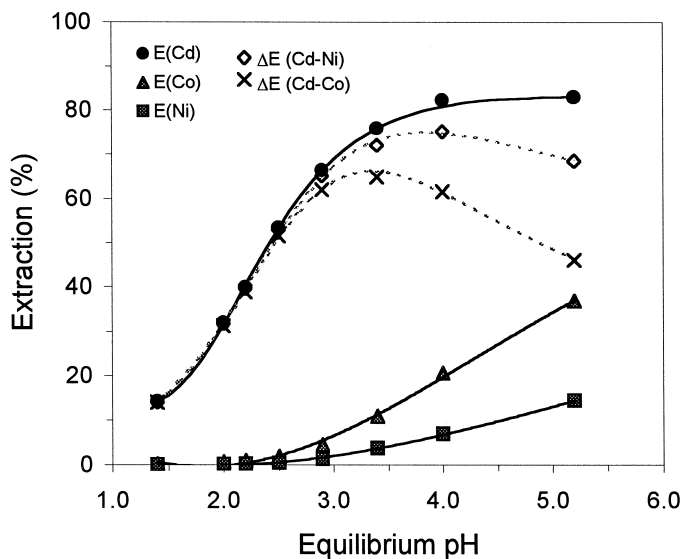| Cyanex 272 concentration	Single contact, O/A = 1			Cobalt loading capacity g/l
	% Extraction		$\beta_{Co/Ni}$	
	Co	Ni		
0.10 M	29	0.05	800	–
0.25 M	70	0.2	1150	2.5
0.50 M	90	0.8	1100	4.5
0.75 M	92	3	350	–

Fig. 3. Extraction percentages of Cd, Co and Ni and respective extraction differences (ΔE) with 1 M DEHPA, as a function of the pH; initial aqueous solution: 80 g/l Ni, 30 g/l Cd and 3 g/l Co; O/A = 1.

solutions containing different cobalt concentrations (1 and 3 g/l) and the same nickel concentration (80 g/l) were examined. Therefore, the concentrations of cobalt foreseen for the leach solutions of the process are covered by this study.
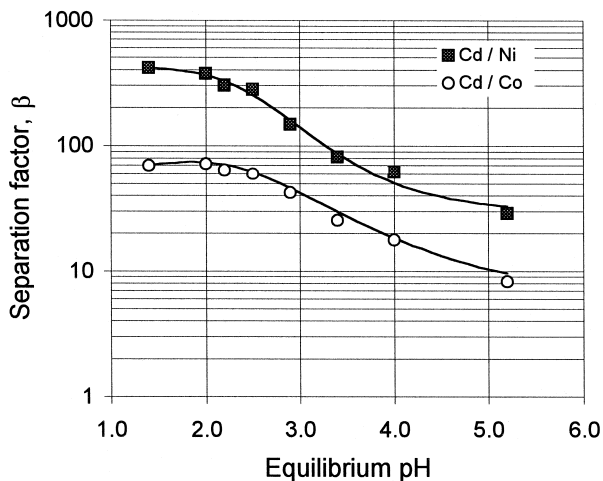

Fig. 4. Separation factors Cd/Co and Cd/Ni with 1 M DEHPA, as a function of the pH; initial aqueous solution: 80 g/l Ni, 30 g/l Cd, and 3 g/l Co; O/A = 1.
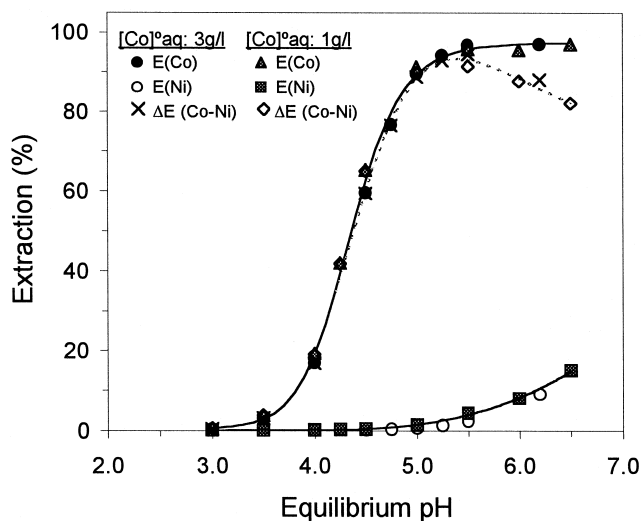
Fig. 5. Extraction percentages of Co and Ni and respective extraction differences (ΔE) with 0.5 M Cyanex 272, as a function of the pH; initial aqueous solution: 80 g/l Ni and 1 or 3 g/l Co; O/A = 1.

The extraction of cobalt and nickel is practically independent of the cobalt concentration in the aqueous phase within the range tested. The maximum value of the extraction difference $\Delta E_{Co-Ni} = E_{Co} - E_{Ni}$ was established at pH 5–5.5, according to the Fig. 5.
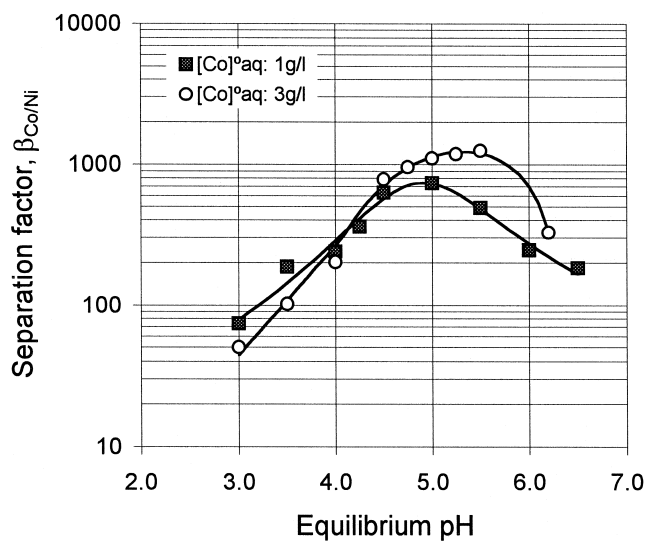

Fig. 6. Separation factors Co/Ni with 0.5 M Cyanes 272, as a function of the pH; initial aqueous solution: 80 g/l Ni and 1 or 3 g/l Co; O/A = 1.

So 5–5.5 was considered the optimised pH range for extraction. The separation factors for this series of trials are presented in the Fig. 6. The highest β values are in a similar pH range (5–5.5) of the maximum ΔE_{Co-Ni} previously determined. So both parameters led to the same optimised solution. In this case, the separation factors are not very far from those previously obtained with diluted solutions (Fig. 2). The reasons for that can be attributed to the equivalent cobalt concentrations in the two solutions despite nickel concentration being considerably different. This indicates that Cyanex 272 is in fact very selective for cobalt even at elevated concentrations of nickel.

4. Equilibrium data in the cadmium separation circuit

The equilibrium data in extraction, scrubbing and stripping operations of the cadmium circuit were determined. Subsequently the resulting overall solvent extraction circuit was simulated.

4.1. Extraction isotherms

The extraction isotherms for cadmium are plotted in the Fig. 7. 1 M DEHPA and a feed solution containing about 80 g/l Ni, 30 g/l Cd and 3 g/l Co were used at controlled pH. Only the most unfavourable cobalt concentration (3 g/l) was considered. The influence of pH on the extraction efficiency is negligible at lower cadmium concentrations but becomes relevant at higher concentrations. Maximum loading capaci-
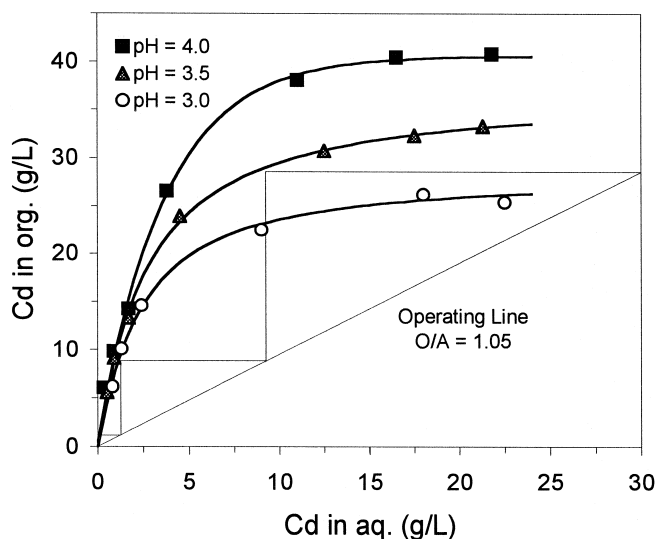

Fig. 7. Extraction equilibrium isotherms of cadmium with 1 M DEHPA at different pH values, from an initial aqueous solution containing 80 g/l Ni, 30 g/l Cd and 3 g/l Co.

ties for cadmium of 27 g/l at pH = 3, of 33 g/l at pH = 3.5 and of 40 g/l at pH = 4 were attained.

The distribution data for the other two metals were also determined (Fig. 8) to correlate the level of contamination of the solvent with the cadmium concentration in it. It is clear that the cobalt and the nickel co-extracted are minimised when cadmium concentration attains its maximum value. For example, at pH 3.5 the concentration of cadmium in the organic phase is 33 g/l while the concentrations of cobalt and nickel are reduced to 0.10 and 0.40 g/l, respectively.

From the above equilibrium data a simulation of a stage-by-stage countercurrent circuit for cadmium was carried out. The McCabe–Thiele construction at pH 3.5 is shown in Fig. 7. The criteria used in phase ratio optimisation was to achieve a compromise between 3 objectives: (1) the maximum recovery of the metal; (2) the maximum concentration of this metal in the organic phase and (3) the minimum contamination by the other metals present. This resulted in phase ratio O/A = 1.05. These conditions allow obtaining a final cadmium raffinate with 0.09 g/l and a loaded organic with 29 g/l of cadmium. An overall cadmium recovery of 99.7% can therefore be foreseen from this simulation.

The co-extraction of cobalt and nickel can be derived from Fig. 8. For a cadmium concentration of 29 g/l in the organic, at pH = 3.5, a contamination of 0.25 g/l of cobalt and 1.5 g/l of nickel can be expected. These values could be reduced using lower phase ratios but the cadmium recovery would be strongly affected. The best option to overcome this problem was to maximise the cadmium recovery and to introduce a scrubbing operation to improve the purity of the organic phase.
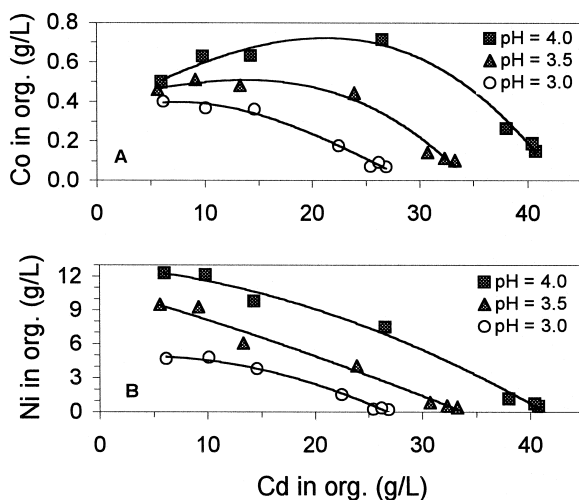

Fig. 8. Correlation between the cobalt (A) and nickel (B) co-extracted into the organic phase and the respective equilibrium cadmium concentration; initial organic: 1 M DEHPA; initial aqueous solution: 80 g/l Ni, 30 g/l Cd and 3 g/l Co.

4.2. Scrubbing and stripping isotherms

The scrubbing of nickel and cobalt from the cadmium-loaded organic was accomplished with a small volume of a pure cadmium aqueous solution. So, an ionic change of cadmium with the cobalt and nickel co-extracted in the organic phase was expected. A scrubbing solution containing 30 g/l Cd was used. The outlet scrub solution is to be in principle recycled to the extraction section and mixed with the feed solution, without significantly changing its cadmium concentration.

For the scrubbing studies the solvent (1 M DEHPA) was previously loaded with cadmium. The aim of this operation was to generate, in a single stage, an organic phase as similar as possible to the loaded organic leaving the countercurrent extraction unit. This was achieved by choosing the appropriate phase ratio from the extraction equilibrium data previously determined. Two loaded organic phases were then prepared, the first one by contacting the fresh solvent with an aqueous solution containing 80 g/l Ni, 30 g/l Cd ad 3 g/l Co at pH = 3.5 and at a phase ratio O/A = 1/5. An organic phase with 33 g/l Cd, 0.05 g/l Co and 0.56 g/l Ni was obtained. The second one was loaded by contacting fresh solvent with an equivalent feed solution at the same pH and at a different phase ratio, O/A = 2/3. A loaded organic containing 28 g/l Cd, 0.23 g/l Co and 1.1 g/l Ni was obtained in this case.

The scrubbing isotherms are plotted in Figs. 9 and 10. The type of curves obtained showed that scrubbing of nickel is very efficient while cobalt removal is not so easy. The graphical simulation shows that in two stages nickel can be reduced in the organic
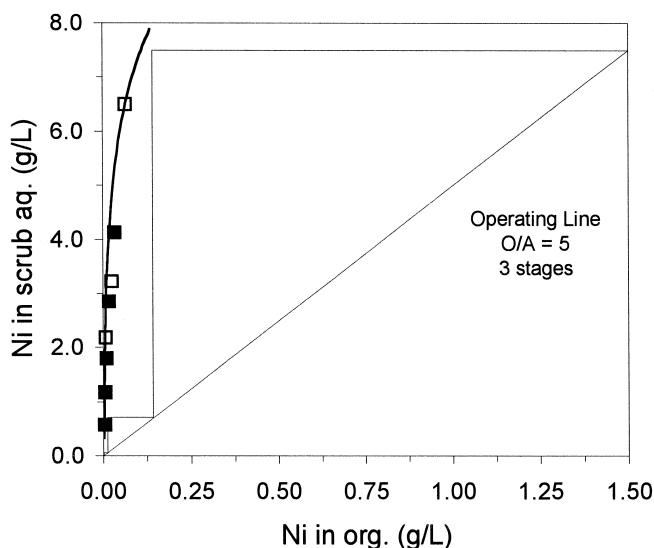

Fig. 9. Equilibrium isotherms for nickel scrubbing from loaded 1 M DEHPA with a cadmium solution assaying 30 g/l Cd. Initial loading of the phase: 33 g/l Cd, 0.05 g/l Co, 0.56 g/l Ni (full symbols) or 28 g/l Cd, 0.23 g/l Co, 1.1 g/l Ni (empty symbols).
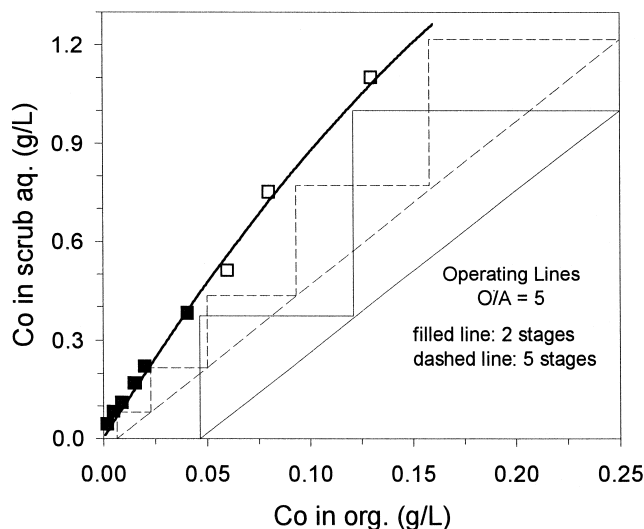
Fig. 10. Equilibrium isotherms for cobalt scrubbing from loaded 1 M DEHPA with a cadmium solution assaying 30 g/l Cd. Initial loading of the organic phase: 33 g/l Cd, 0.05 g/l Co, 0.56 g/l Ni (full symbols) or 28 g/l Cd, 0.23 g/l Co, 1.1 g/l Ni (empty symbols).

phase from 1.5 g/l to 0.012 g/l while cobalt decreases from 0.25 g/l to 0.046 g/l. A third stage reduces nickel concentration to 1 mg/l. To attain lower levels of cobalt it is however necessary to use a larger number of stages (5 stages can allow cobalt reduction to 7 mg/l).
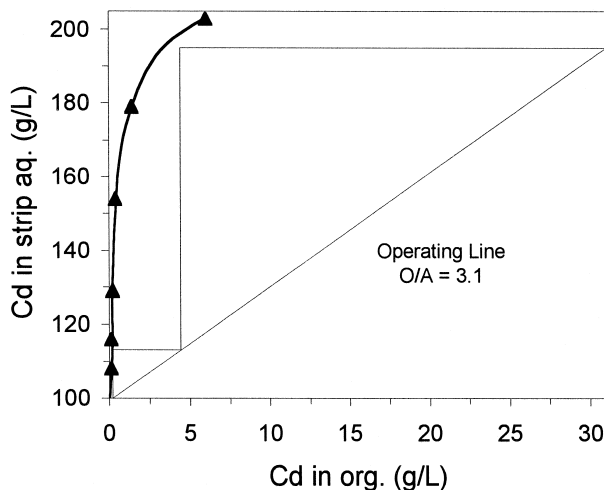

Fig. 11. Stripping equilibrium isotherm for cadmium from loaded 1 M DEHPA with a stripping solution containing 1 M H_2SO_4 and 100 g/l Cd. Initial loading of the organic phase: 27 g/l Cd.

Table 5
The cadmium recovery circuit: prediction of the main stream compositions and recovery yields. Organic phase: 1 M DEHPA; scrub solution: 30 g/l Cd; strip solution: 1 M H_2SO_4 + 100 g/l Cd

	Extraction section—3 stages, pH = 3.5, O/A = 1.05			Scrubbing section—2 stages, O/A = 5	Stripping section—2 stages, O/A = 3.1	
	Feed	Raffinate	Loaded organic	Scrubbed organic	Stripped organic	Strip liquor
Cd, g/l	30	0.09	29	31	0.21	195
Co, g/l	3	2.8	0.25	0.046	–	0.14
Ni, g/l	80	79	1.5	0.012	–	0.04
Process efficiency	Cd extraction = 99.7%			Co scrubbed = 82% Ni scrubbed = 99%	Cd stripping = 99.3%	

The following studies were performed in order to evaluate the efficiency of cadmium stripping. A stripping isotherm was determined using as stripping solution 1 M H_2SO_4 already containing 100 g/l Cd (Fig. 11). The use of a highly concentrated cadmium solution for stripping will allow obtaining very concentrated strip liquor, so favouring the economy of cadmium recovery.

From the graphical simulation it can be concluded that only two stages at an optimised phase ratio of O/A = 3.1 will remove more than 99% of the cadmium from the loaded solvent (from 31 g/l to 0.21 g/l), producing simultaneously a concentrated strip liquor assaying 195 g/l Cd.

The extraction, scrubbing and stripping studies reported up to now have led to the conclusion that it is possible to recover cadmium efficiently from typical leach solutions coming from the hydrometallurgical processing of Ni–Cd batteries. Table 5 summarises the main results obtained.

5. Equilibrium data in the cobalt separation circuit

5.1. Extraction isotherms

The extraction of cobalt and its separation from nickel could be attained using the extractant 0.5 M Cyanex 272 at pH 5–5.5. The extraction equilibrium data were determined with a typical aqueous process solution containing 80 g/l Ni, 1 and 3 g/l Co and the expected cadmium remaining in the raffinate of the first circuit (maximum about 0.1 g/l Cd). The extraction pH was maintained constant by adding a few drops of a sodium hydroxide solution. For the solution containing 3 g/l Co two isotherms were obtained, at pH 5 and at pH 5.5 (Fig. 12). At pH 5 the maximum loading capacity is 4.5 g/l while at pH 5.5 it is 8 g/l Co. Therefore the upper pH value was selected to obtain a higher cobalt recovery together with a higher cobalt concentration in the organic phase.

For the feed solution containing 1 g/l Co only one isotherm was determined at pH = 5.2, since in this case the selectivity decreases when the pH approaches 5.5
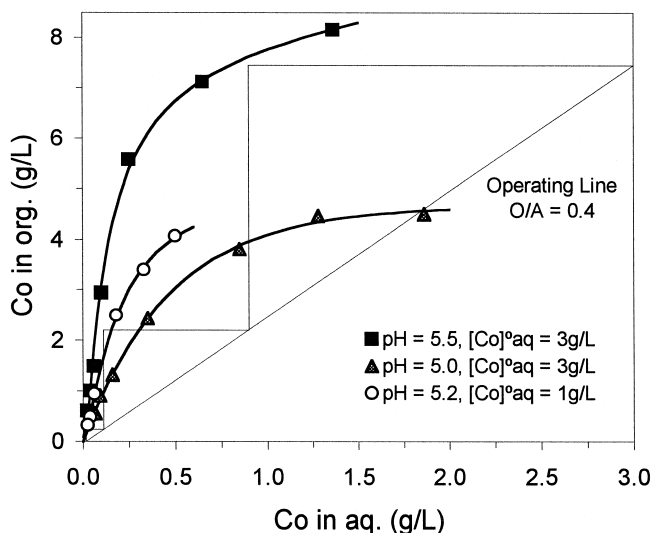
Fig. 12. Extraction equilibrium isotherms of cobalt with 0.5 M Cyanex 272 at different pH values, from an initial aqueous solution containing 80 g/l Ni, 1–3 g/l Co and 0.10 g/l Cd.

(Fig. 6). The isotherm is also plotted in the Fig. 12 and lies between the other two isotherms, indicating that the cobalt concentration in the aqueous phase, within the limits tested, does not markedly affect the isotherm trend.

The equilibrium data for the other metals are presented in the Fig. 13. As for the previous circuit the results are presented in terms of a correlation between the concentrations of the contaminating metals (Ni, Cd) in the organic phase and the cobalt loading in the same phase. In the case of nickel it can be said that Co/Ni selectivity is considerably improved when the cobalt loading increases. For the highest cobalt concentrations obtained, which were 4.5 g/l at pH 5 and 8.2 g/l at pH 5.5, the minimum nickel concentrations achieved were 0.21 g/l and 0.34 g/l respectively.

Cadmium behaviour is totally different because its concentration in the organic phase increases with cobalt. This is a case of lack of selectivity, which was expected because Cyanex 272 extracts both metals. When the cobalt concentration in the aqueous feed is lower (1 g/l) the contamination of cadmium in the organic phase is higher. From these results it can be concluded that cadmium recovery with DEHPA in the first circuit should be maximised in order to avoid further contamination of the cobalt stream with cadmium in the second circuit.

Fig. 12 shows a 3-stage countercurrent extraction at pH 5.5. Using the optimised phase ratio O/A = 0.4 it is possible to obtain a raffinate with 0.016 g/l Co from a feed solution containing 3 g/l Co. Simultaneously a cobalt loading in the organic phase of 7.5 g/l can be anticipated.

The nickel contamination in the loaded organic phase can be estimated from Fig. 13. This approach can be used since the slope of the curves is negative which suggests that the cobalt loading determines the equilibrium of nickel. Therefore the nickel in the
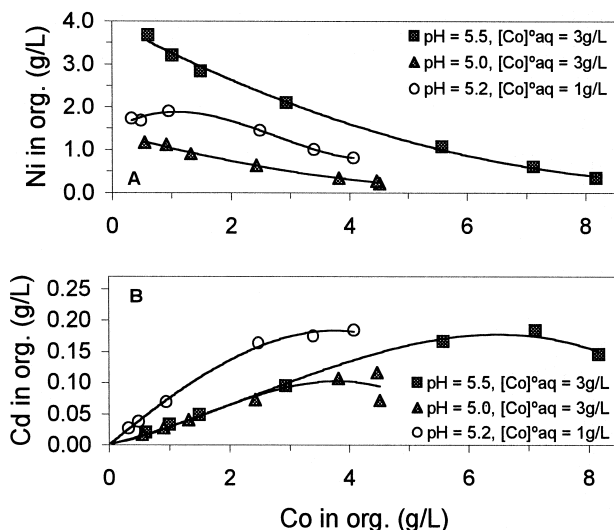
Fig. 13. Correlation between the nickel (A) and cadmium (B) co-extracted into the organic phase and the respective equilibrium cobalt concentration; initial organic: 0.5 M Cyanex 272; initial aqueous solution: 80 g/l Ni, 1–3 g/l Co and 0.10 g/l Cd.

organic phase leaving the extraction section would be 0.50 g/l, which is the maximum nickel concentration for a cobalt loading of 7.5 g/l. The relation Cd/Co is in contrast an ascent curve (Fig. 13) and so the concentration of cadmium in organic cannot be directly derived from that correlation. What we can eventually guarantee is that the maximum cadmium concentration in the organic will be the maximum value obtained in the equilibrium data of the figure, i.e., 0.18 g/l. As in the case of the cadmium circuit, the way to minimise cobalt contamination with nickel and cadmium was to scrub the loaded solvent with a cobalt solution.

5.2. Scrubbing and stripping isotherms

The organic phase for scrubbing tests (0.5 M Cyanex 272) was previously loaded with cobalt in a single contact with the aqueous feed containing 80 g/l Ni, 3 g/l Co and 0.10 g/l Cd, at pH 5.5 and at a phase ratio O/A = 1/3. The resulting organic phase assayed 6.8 g/l Co, 0.75 g/l of Ni and 0.15 g/l Cd. The scrubbing solution used contained 6 g/l of cobalt.

It can be seen from Fig. 14 that the major part of the nickel contaminating the organic phase can be easily removed. The nickel concentration can be reduced from 0.5 g/l to 0.02 g/l (96% removal). The scrubbing of cadmium was more problematic since the equilibrium data generated (Table 6) show that cadmium removal from the organic phase is very poor, even using unpractical lower phase ratios (maximum value of 60% removal attained at O/A = 1/2).

The selected cobalt concentration in the scrubbing solution can now be explained. In the simulated circuit, the nickel concentration in the organic phase is reduced from 0.50
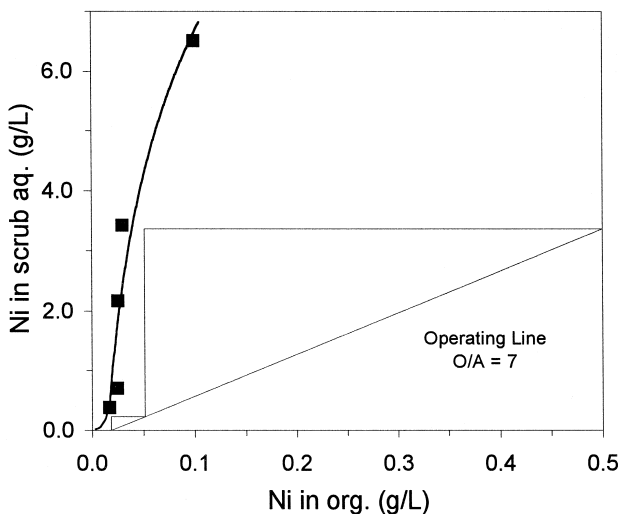
Fig. 14. Scrubbing equilibrium isotherm of nickel from loaded 0.5 M Cyanex 272 with a cobalt solution containing 6 g/l Co; initial loading of the organic phase: 6.8 g/l Co, 0.75 g/l Ni, and 0.15 g/l Cd.

g/l to 0.02 g/l. For the phase ratio proposed (O/A = 7/1) this value is equivalent to a cobalt variation in the scrub solution of 3.4 g/l. Using a scrubbing solution with 6 g/l the scrub raffinate will contain 2.6 g/l which is very close to the cobalt concentration in the feed solution. Thus this scrubbing raffinate can be recycled back to the extraction section without any significant change in the cobalt extraction conditions.

Cobalt stripping was studied using a concentrated stripping solution containing 0.5 M H_2SO_4 and 100 g/l Co to allow obtaining saturated strip liquors for crystallisation. The isotherm and the process for an initial organic phase containing 8 g/l Co are shown in Fig. 15. An efficient recovery of cobalt can be achieved together with the production of very concentrated strip liquors containing 126 g/l Co.

It can be said that Cyanex 272 is adequate to recover cobalt from the cadmium-free solutions coming from hydrometallurgical processing of spent Ni–Cd batteries. Table 7 shows the typical features and concentrations of the separation process.

Table 6
Scrubbing equilibrium data of cadmium with a scrub solution containing 6 g/l Co from an organic phase (0.5 M Cyanex 272) loaded with 6.8 g/l Co, 0.75 g/l Ni and 0.15 g/l Cd

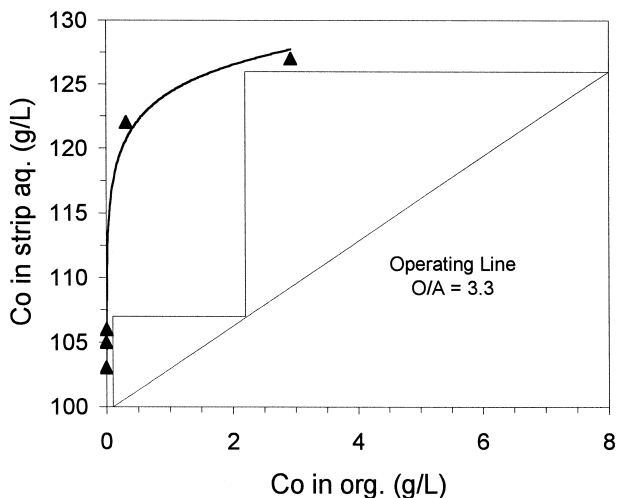| O/A	Cadmium concentration (g/l)	
	Organic phase	Aqueous phase
1/2	0.06	0.04
1/1	0.09	0.06
3/1	0.13	0.06
5/1	0.14	0.025
10/1	0.14	0.010

Fig. 15. Stripping equilibrium isotherm of cobalt from loaded 0.5 M Cyanex 272 with a stripping solution containing 0.5 M H_2SO_4 and 100 g/l Co; initial loading of the organic phase: 7.3 g/l Co.

The efficiency of cobalt recovery is generally high. The sole problem is the contamination of the cobalt with the remaining cadmium. It must be stressed though that the residual cadmium, even minimised in the cadmium circuit, will contaminate the cobalt in the second circuit. However it is expected that, during cobalt crystallisation, cadmium will probably remain in the mother-liquors.

Another important aspect to stress is that the simulations were made considering a pure cobalt stripping solution. Nevertheless in a real process the strip liquor coming from cobalt recovery would have to be recycled and the level of impurities would build up. So the quality of the cobalt product will be affected and some additional means of impurity removal should be applied. A similar situation can happen in the cadmium circuit. All these aspects need to be studied in the future.

Table 7
The cobalt recovery circuit: prediction of the main stream compositions and recovery yields. Organic phase: 0.5 M Cyanex 272; scrub solution: 6 g/l Co; strip solution: 0.5 M H_2SO_4 + 100 g/l Co

	Extraction section—3 stages, pH = 5.5, O/A = 0.4			Scrubbing section—2 stages, O/A = 7	Stripping section—2 stages, O/A = 3.3	
	Feed	Raffinate	Loaded organic	Scrubbed organic	Stripped organic	Strip liquor
Co, g/l	3	0.016	7.5	8	0.10	126
Ni, g/l	80	80	0.5	0.02	–	0.07
Cd, g/l	0.10	0.04	0.15	0.15	–	0.5
Process efficiency	Co extraction = 99.5%			Ni scrubbed = 96% Cd scrubbed ∼ 0	Co stripping = 98.8%	

6. Conclusions

In this work a solvent extraction process for the separation of cadmium, cobalt and nickel was developed, using two circuits: the cadmium separation circuit using 1 M DEHPA as extractant and the cobalt separation circuit using 0.5 M Cyanex 272. It was shown that these two extractants were more efficient and selective than the competitor Ionquest 801. Under optimised conditions it was concluded that in the cadmium circuit a recovery of 99.7% of the cadmium is achieved and an organic phase containing about 30 g/l Cd is produced. After efficient scrubbing with a pure cadmium scrubbing solution this metal is recovered by stripping in such conditions that a strip liquor containing 195 g/l Cd, 0.14 g/l Co and 0.04 g/l Ni is produced and cadmium is recovered from it without appreciable contamination. The raffinate from this separation step is therefore processed in the cobalt circuit. The experimental work carried out showed that in this circuit a recovery of 99.5% of the cobalt is attained and a loaded organic phase containing near 8 g/l Co is produced. After scrubbing, now with a pure cobalt aqueous solution, the cobalt is recovered by stripping, generating a strip liquor with 126 g/l Co, 0.07 g/l Ni and 0.5 g/l Cd. The cadmium not removed in the first circuit was found to be the most important impurity contained in the three separated metal streams.

The process is now being tested continuously in a bench-scale mixer–settler. The technology seems promising allowing the production of pure metal streams from which valuable commercial products can be produced. In the case of cadmium, which is a low-value metal, it appears unlikely that solvent extraction could be economic but the environmental advantages over the classic pyrometallurgical processes could justify its use. This will undoubtedly lead to more efficient management of nickel–cadmium wastes.

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